

Simulation study on copper and zinc release from contaminated sandy soils due to acidification

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Abstract: Afforestation in sandy soils can cause soil acidification and affect Cu and Zn release. The behaviors of Cu and Zn release from contaminated arable sandy soils were investigated in the laboratory with the methods of simulated acidification of the soils. The results showed that soil acidification could change chemical forms of Cu and Zn in the soils, impel the transformation of Cu and Zn from carbonate associated fractions to exchangeable, organic matter and oxides associated fractions, and thus increase the release potential of Cu and Zn in the soils. The effect of the acidification on Zn leaching was more significant than that of Cu. Water solubility of Cu and Zn in the soils was increased with decreasing pH, and the solubility of Cu and Zn was increased exponentially at pH 3.8–4.5, and 6.2–6.5, respectively.

Keywords: Copper; Zinc; Contaminated sandy soil; Acidification; Afforestation

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Introduction

The repeated applications of chemical fertilizer, organic manures, municipal waste, fungicides, and pesticides to soils are likely to result in heavy metal accumulation in soils (Payne *et al.* 1988; Kingery *et al.* 1994; van der Watt *et al.* 1994; Moore *et al.* 1998), and thus increase potential contamination of surface and groundwater with heavy metals through runoff and leaching (Purves 1985; Alloway 1995; Moore *et al.* 1998). When accumulation of heavy metals in soils limits crop growth, the contaminated soils shall not be used for crop production and transformed into forest land. However, afforestation of agricultural land leads to major changes of the chemical conditions in the soils and a decrease of pH in soil due to termination of regular lime applications and increased production of organic acid in the litter (Johnston *et al.* 1986). The solubility of heavy metals in soils is mainly influenced by pH (McBride *et al.* 1997), therefore, acidification induced by afforestation may increase solubility of heavy metals in the contaminated soils. This is special true for sandy soils, because of a low buffering capacity of the sandy soils.

Sandy spodosols are representative soils in Florida, USA. Under natural conditions with plantation of sand pine [*Pinus clausa* (Chapm) vasey], these soils are strong acid with pH < 5.0, but they do not pose a significant risk of soil heavy metal runoff, because of low background of heavy metals in the case. However, soils under citrus production were commonly contaminated with high concentrations of Cu and Zn due to long-term application of fertilizers and pesticides (Alva 1992). It is concerned for fate of Cu and Zn accumulated in the soils, when land use is trans-

formed to forest and lime materials are no longer applied. Therefore, the objective of this study is to examine the changes of forms and solubility of Cu and Zn accumulated in the sandy soils following a simulated acidification.

Materials and methods

Soil sampling and chemical-physical analysis

Three surface soil samples (0–5 cm deep) were selected and collected from different commercial citrus groves in St. Lucie County, Florida, USA. All of the soils are classified as Wabasso (sandy, siliceous, hyperthermic Alfic Haplaquods). Soil samples were air-dried and a sub-sample from each sample was passed through a 2-mm sieve for analysis.

Soil pH was measured in water at a ratio of soil to water (1:1) by using a pH/ion/conductivity meter (Accumet Model 50, Fisher Scientific, Norcross, GA), (Spark 1996). Particle composition of soil sample was determined by using the micro-pipette method (Miller *et al.* 1987). Total carbon (C) in the samples was determined by using a CN-Analyzer (Vario MAX CN Macro Elemental Analyzer, Elemental Analysensystem GmbH, Hanau, Germany). All soil samples were sandy soils, and differed widely in their total of Cu and Zn. The Cu and Zn concentrations in the soil samples were significantly higher than those of non-cultivated forest soil with a native population of sand pine (Cu and Zn concentrations in the non-cultivated forest soil were 4.1 mg·g⁻¹ and 6.6 mg·kg⁻¹, respectively), (Zhang *et al.* 2003), (Table 1).

Experiment for effect of pH on water-solubility of copper and zinc in the soils

Each of 2-g soil samples was placed into 50-mL centrifuge tubes. Deionized water of 20 mL was added to each tube. The pH value of the suspensions was adjusted to 1.5 to 8, respectively, by using 1-mol·L⁻¹ HNO₃ or 1-mol·L⁻¹ NaOH. The volume of HNO₃ or NaOH used for pH adjustment was recorded for each tube. Deionized water was added to make for a total of 40 mL solution (ratio of liquid to solid is 20:1). After shaking for 24 h, the suspensions were used for measuring pH and then centrifuged, filtered and analyzed for Cu and Zn concentrations by

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using an Inductively Coupled Plasma Atomic Emission Spec-

trometry (ICP-AES, Ultima, JY Horiba Inc. Edison, N.J.).

Table 1. Characteristics of the tested soils

Sample	pH	Organic C ($\text{g}\cdot\text{kg}^{-1}$)	Total Cu ($\text{mg}\cdot\text{kg}^{-1}$)	Total Zn ($\text{mg}\cdot\text{kg}^{-1}$)	Sand ($\text{g}\cdot\text{kg}^{-1}$)	Silt ($\text{g}\cdot\text{kg}^{-1}$)	Clay ($\text{g}\cdot\text{kg}^{-1}$)
Soil 1(S1)	7.03	12.5	400	101	932	40	28
Soil 2(S2)	7.48	7.9	286	68	903	56	41
Soil 3(S3)	7.27	11.3	306	70	921	36	43

Acidification treatment of the soils

All of the three soil samples (Table 1) were selected for this experiment. For each soil, pH was adjusted to 4.0, 4.5, and 5.0, by using dilute acids (H_2SO_4 : HNO_3 = 1:1). Native soil samples without any treatments were used for control. The pH-adjusted soils were then incubated with 5% moisture at room temperature for 365 days. Each treatment included 2.0-kg soil samples. Three replicates were used for each treatment.

Fractionation of Cu and Zn in the incubated soil samples

The total Cu and Zn in the incubated soils were fractionated into five fractions (exchangeable, carbonate associated, organically associated, oxide associated, and residual fractions) by a modified procedure of Amacher (1996). Two grams of soil were sequentially extracted with $0.1\text{-mol}\cdot\text{L}^{-1}$ $\text{Mg}(\text{NO}_3)_2$, $1\text{-mol}\cdot\text{L}^{-1}$ NaOAc , $0.1\text{-mol}\cdot\text{L}^{-1}$ $\text{Na}_4\text{P}_2\text{O}_7$ and $0.2\text{-mol}\cdot\text{L}^{-1}$ ammonium oxalate + $0.2\text{-mol}\cdot\text{L}^{-1}$ oxalic acid + $0.1\text{-mol}\cdot\text{L}^{-1}$ ascorbic acid (pH3) for separation of exchangeable, carbonate associated, organically associated, and oxides associated fractions. After each extraction, the suspension was centrifuged at $7500\times g$ (rcf, relative centrifuge force) for 30 min and then the supernatant was passed through a Whatman# 42 filter paper. Total and residual Cu and Zn contents in the soils were determined by digesting samples with nitric acid and perchloric acid (Reed *et al.* 1996). Copper and Zn concentrations in the extracts and digested solutions were determined by using the ICP-AES.

Column leaching

Copper and Zn leachabilities of the incubated soils were determined by using soil columns. Each column was prepared in the laboratory by using a plexiglass leaching column (10 cm long and 7.5-cm inner diameter). The bottom of the column was consisted of a plexiglass plate containing several 5-mm-wide holes. The top of the plate was covered with a nylon cloth and glued to the bottom of the column. Each 300-g soil sample was packed to form a column. Two disks of filter paper (Whatman# 2) were placed on the top of soil prior to leachings to prevent disturbance by applied water. Prior to setting up the leaching experiment, the soil columns were slowly saturated from the bottom upward with deionized water to remove air pockets. The columns were then set up in stands for two days at room temperature. About 110 mL (1 pore volume) of deionized water (pH = 7) was applied to each soil column on a daily basis and repeated for ten days at a rate of $2\text{ mL}\cdot\text{min}^{-1}$. This application rate did not allow any ponding on the top of the column. Leachates were collected in 1000-mL beakers below the soil columns, filtered through Whatman# 42 filter paper for analysis. Copper and Zn amounts in the leachate were determined by using the ICP-AES.

Extraction of available Cu and Zn from the incubated soils

Two extraction methods were used to extract soil labile Cu and Zn. (i) deionized water -extractable Cu and Zn (ratio of soil to deionized water was 1:10; 60-min reaction time); (ii) Meh-

lich-1 extractable Cu and Zn [ratio of soil to $0.05\text{-mol}\cdot\text{L}^{-1}$ HCl + $0.0125\text{-mol}\cdot\text{L}^{-1}$ H_2SO_4 was 1:4; 5-min reaction time (Reed and Martens, 1996)]. After each extraction, the suspension was centrifuged at $7500\times g$ relative centrifuge force for 30 min and then the supernatant was passed through a Whatman# 42 filter paper. Copper and Zn amounts in the supernatant after centrifugation were determined by using the ICP-AES.

Results and discussion

Solubility of Cu and Zn in various pH

The water solubility of Cu and Zn in the soils increased with decreasing pH (Fig. 1). The changing rate of Cu and Zn solubility varied with pH values. When pH was at high side, the increase in Cu and Zn solubility with pH was small. As pH decreased to a certain value, the increase of Cu and Zn solubility with pH became significant. The pH values at which sharp increases in the solubility occurred were about 3.8–4.5 for Cu, and 6.0 for Zn. The solubilization of Zn in the soils was more sensitive to change in pH. The results suggest that release of Cu and Zn from the soils increases exponentially when soil acidification makes pH falling to 3.8–4.5 and 6.2–6.5, respectively.

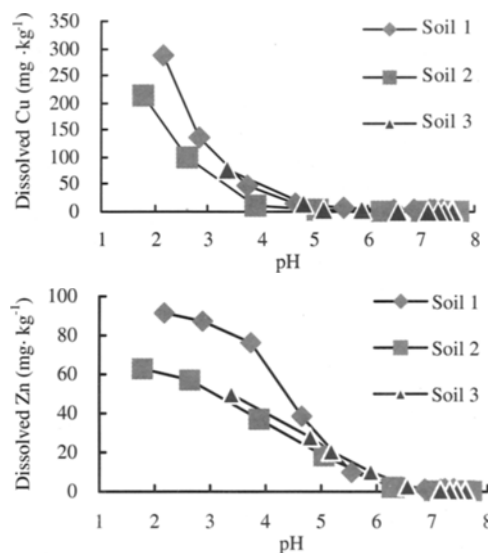


Fig.1. Effect of pH on the water solubility of Cu and Zn in the soils

Effects of pH on copper and zinc forms in the soils

Soil acidification could significantly affect fractions of Cu and Zn in the soils (Table 2). Exchangeable fraction of either Cu or Zn increased significantly with decreasing pH. In contrast, carbonate associated Cu and Zn fraction decreased with decreasing pH. In addition, organic matter and oxides associated Cu and Zn fractions tended to increase with decreasing pH. The percentages of residual Cu and Zn fraction in the acidified soils was constant or changed slightly as compared with those of the control soils. The results indicated that carbonate associated fraction of Cu and Zn was transformed into exchangeable, organic matter and ox-

ides associated fractions when soils were acidified. The effects of pH on change of exchangeable Zn fraction in the soils were significantly more than those of Cu. When pH was decreased to 4.0, exchangeable Zn fraction increased as much as 7.3–9.0 times of that of the controls, whereas exchangeable Cu fraction increased as much as 1.6–3.0 times of that of the controls. Exchangeable

fraction of metals had much higher bio-availability than carbonate associated fraction of the metals (Amacher 1996). Therefore, increased exchangeable fraction and decreased carbonate associated fraction of the metals due to soil acidification could elevate release potential of the two metals from the soils.

Table 2. Effects of pH on fractions of Cu and Zn in the soils

Sample	pH value	Cu (%)					Zn (%)				
		F ₁	F ₂	F ₃	F ₄	F ₅	F ₁	F ₂	F ₃	F ₄	F ₅
Soil 1 (S1)	Control	1.2c ^a	29.8a	56.5c	9.2c	3.3a	2.1c	42.0a	39.6b	10.6b	5.6a
	5.0	1.2c	20.7b	63.7b	10.7bc	3.7a	2.9c	24.0b	56.5a	12.0b	4.6a
	4.5	1.6b	16.4c	65.3ab	11.8b	4.9a	7.0b	19.2c	54.8a	15.4a	3.6a
	4.0	1.9a	10.6d	68.4a	14.1a	5.0a	15.3a	11.4d	50.3a	17.6a	5.4a
Soil 2 (S2)	Control	0.4b	18.8a	58.0b	12.5c	10.3a	1.2c	33.8a	36.1b	19.4c	9.6a
	5.0	0.7ab	16.1a	58.4b	14.2b	10.6a	1.2c	26.2b	39.1ab	20.1bc	13.4a
	4.5	0.8ab	12.7b	59.5b	16.8a	10.2a	3.1b	21.6b	43.4a	22.7b	9.2a
	4.0	1.0a	5.7c	66.4a	17.7a	9.2a	10.8a	12.9c	40.0a	26.0a	10.3a
Soil 3 (S3)	Control	0.4b	21.2a	62.1c	10.1c	6.1a	1.7c	39.9a	32.9c	5.6c	19.9a
	5.0	1.1a	17.7b	62.2c	12.1b	6.9a	3.7bc	28.4b	42.3b	7.2bc	18.4ab
	4.5	1.0a	13.7b	65.4b	13.4ab	6.5a	5.6b	22.8c	40.3b	9.4b	21.9a
	4.0	1.2a	6.9c	70.5a	15.3a	6.1a	12.4a	14.7d	44.6a	12.1a	16.2b

Notes: F₁---- Exchangeable fraction; F₂---- Carbonate-associated fraction; F₃---- Organic matter associated fraction; F₄---- Oxides associated fraction; F₅---- Residual fraction. ^a, mean within a column with the same letter(s) are not significantly difference at $p = 0.05$ probability level, statistical comparisons were made between treatments with S1 or S2 or S3 (separately).

Effects of pH on available Cu and Zn in the soils

Amounts of water-soluble and Mehlich 1-extractable Cu and Zn can be used as indexes for evaluating mobility of Cu and Zn in the sandy soils (Zhang et al. 2003). Amount of water-soluble Cu and Zn is an intensity indicator that is related directly with Cu and Zn concentrations in soil solution, whereas amount of Mehlich 1-extractable Cu and Zn could reflect total potential of Cu and Zn released from the soils. On average, the amounts of Mehlich 1-extractable Cu accounted for 38.4%, 35.9%, and 40.6% of total amounts of Cu in the S1, S2, and S3, and the

Mehlich 1-extractable Zn accounted for 86.7%, 71.7%, and 48.1% of total Zn amounts in the S1, S2, and S3, respectively. The proportions of the total Zn amounts as available fraction were greater than those of Cu. The amounts of Mehlich 1-extractable Cu were about 23–35, 40–78, and 38–104 times, respectively, of water soluble Cu amounts for S1, S2, and S3 (Fig. 2). The amounts of Mehlich 1-extractable Zn were 16–57, 20–131, and 12–151 times, respectively, of water soluble Zn amount for S1, S2, and S3.

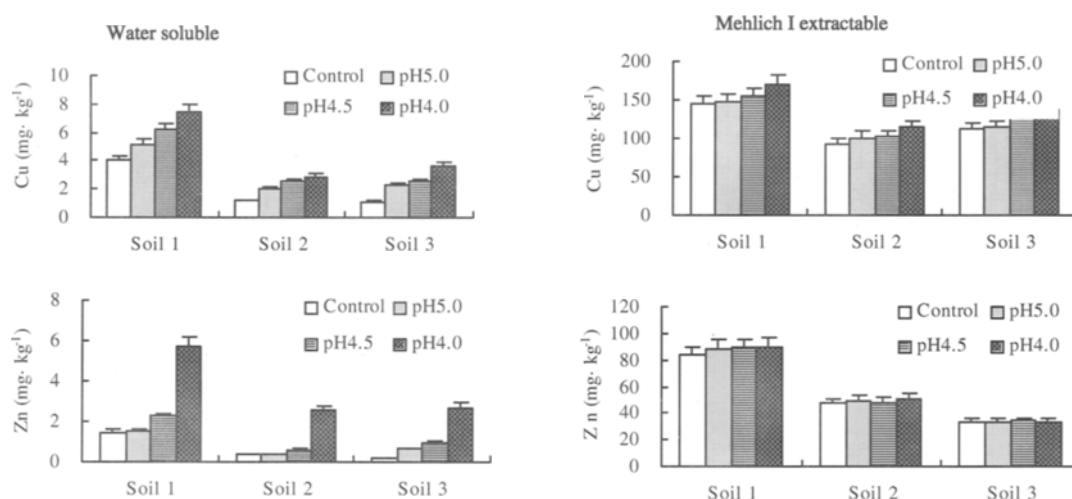


Fig. 2 Effects of acidification on water-soluble and Mehlich 1-extractable Cu and Zn in the soils

Soil acidification increased slightly Mehlich 1-extractable Cu and Zn. When pH was decreased to 4.0, amounts of Mehlich 1-extractable Cu and Zn in the soils increased to 1.18–1.22 and 1.01–1.06 times of those in their control soils, respectively. However, soil acidification increased significantly water-soluble Cu and Zn amounts. The amounts of water-soluble Cu at pH 5.0, 4.5, and 4.0 were 1.25–2.08, 1.53–2.36, and 1.83–3.32 times of

that in the control soil sample. The amounts of water-soluble Zn at pH 5.0, 4.5, and 4.0 were 1.22–2.86, 1.53–4.54, and 3.88–12.23 times of that in the control soil sample. The ratio of water soluble Cu (or Zn) to the Mehlich 1-extractable Cu (or Zn) increased significantly with decreasing pH. The results indicated that pH had slightly effects on total potential of releasable Cu

and Zn in the soils, but it had significant effects on intensity of Cu and Zn released from the soils.

Effects of pH on leachability of Cu and Zn in the soils

Acidification increased leaching potentials of Cu and Zn in the soils (Fig. 3). When pH of the soils was decreased to 5.0, 4.5, and 4.0, the amounts of Zn in the first leachates increased to 4.0–7.5, 22.5–34.0, and 131–157 times of those in the control soils, respectively. The accumulated amounts of Zn leached from the soils in all 10 cycles of leaching at pH 5.0, 4.5, and 4.0 reached to 1.85–3.60, 5.77–11.3, and 27.0–38.2 times of those in the control soils, respectively. The influence of pH on leaching of Cu was weaker than on that of Zn. When pH was decreased to 5.0, 4.5, and 4.0, the amounts of Cu in the first leachates increased to 2.36–3.42, 2.64–5.63, and 5.23–7.74 times of those in the control soils, respectively. The accumulated amounts of Cu leached from the soils in 10 leachings at pH 5.0, 4.5, and 4.0 reached to 1.55–2.35, 2.11–3.24, and 2.47–3.47 times of those in the control soils, respectively. Higher accumulated amounts of the metals leached from the soils at decreased pH indicated that decreasing pH could result in more transport of the metals from

the soils. Zinc was more sensitive to be leached than Cu. Most of leached Zn occurred in the first leaching, and the accumulated amounts of Zn were closed to maximum values at the third or fourth leaching (Fig. 3). In contrast, the amounts of Cu in the leachates decreased slowly with increasing number of leaching, and the accumulated amounts of Cu leached from the soils increased gradually with number of leaching.

Afforestation of cultivated soils could decrease soil pH two units within 10–20 years (Jug, *et al.* 1999) or 100 years after afforestation (Johnston *et al.* 1986). If the change of soil pH induced by afforestation influence the release of Cu and Zn from the soils in a similar mechanism as observed in this experiment, a decrease in pH will increase the Cu and Zn release. Consequently, afforestation of the cultivated soils will lead to leaching of Cu and Zn with percolating water to deeper soil layers, which will result in pollution of shallow groundwater with Cu and Zn. On the basis of observation above, it can be concluded that Zn will be leached first during the process of soil acidification. High amount of Zn leached from the soils will occur at pH < 6.0, and high amount of Cu leached from the soils will occur at pH < 4.5.

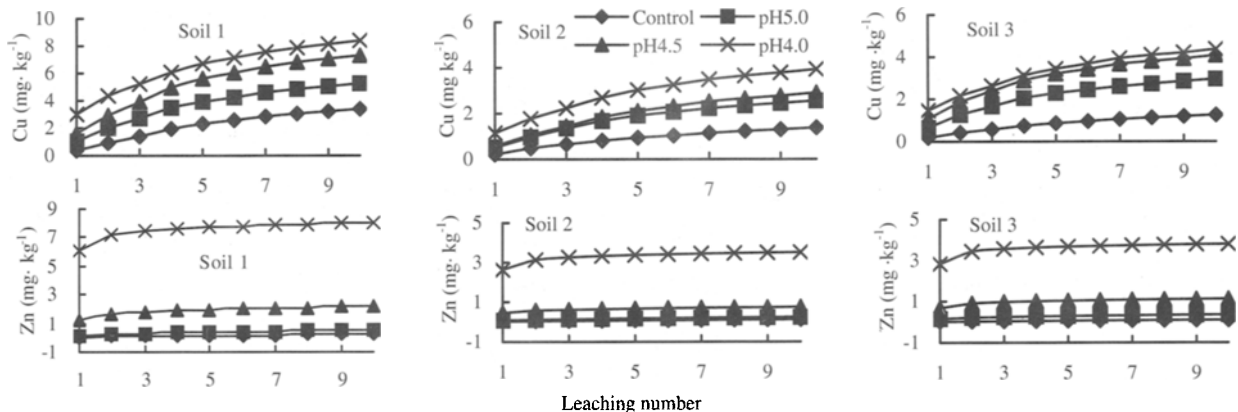


Fig. 3 Accumulated amounts of Cu and Zn released from the soils as a function of leaching number

Conclusions

Water solubility of Cu and Zn in the soils was increased with decreasing pH, and the solubility of Cu and Zn was increased exponentially at pH 3.8–4.5 and 6.2–6.5, respectively. Carbonate associated fractions of Cu and Zn tended to be transformed into exchangeable, organic matter and oxides associated fractions when soils were acidified. The pH had little effects on total available Cu and Zn (Mehlich I extractable) released from the soils, but it had significant effects on water soluble Cu and Zn. Therefore, acidification could increase concentrations of Cu and Zn in runoff from the sandy soils. Zinc was more sensitive to be leached than Cu when pH decreased.

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